Journal of Nuclear Materials 462 (2015) 250–257

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Modeling precipitation thermodynamics and kinetics in type 316 austenitic stainless steels with varying composition as an initial step toward predicting phase stability during irradiation

Jae-Hyeok Shim [a,b,*], Erwin Povoden-Karadeniz [c], Ernst Kozeschnik [d], Brian D. Wirth [a]

[a] Department of Nuclear Engineering, University of Tennessee, Knoxville, TN 37996, USA
[b] High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
[c] Christian Doppler Laboratory for Early Stages of Precipitation, Vienna University of Technology, A-1040 Vienna, Austria
[d] Institute of Materials Science and Technology, Vienna University of Technology, A-1040 Vienna, Austria

HIGHLIGHTS

- We model the precipitation kinetics in irradiated 316 austenitic stainless steels.
- Radiation-induced phases are predicted to form at over 10 dpa segregation conditions.
- The Si content is the most critical for the formation of radiation-induced phases.

ARTICLE INFO

Article history:
Received 9 June 2014
Accepted 7 April 2015
Available online 16 April 2015

ABSTRACT

The long-term evolution of precipitates in type 316 austenitic stainless steels at 400 °C has been simulated using a numerical model based on classical nucleation theory and the thermodynamic extremum principle. Particular attention has been paid to the precipitation of radiation-induced phases such as γ′ and G phases. In addition to the original compositions, the compositions for radiation-induced segregation at a dose level of 5, 10 or 20 dpa have been used in the simulation. In a 316 austenitic stainless steel, γ′ appears as the main precipitate with a small amount of G phase forming at 10 and 20 dpa. On the other hand, G phase becomes relatively dominant over γ′ at the same dose levels in a Ti-stabilized 316 austenitic stainless steel, which tends to suppress the formation of γ′. Among the segregated alloying elements, the concentration of Si seems to be the most critical for the formation of radiation-induced phases. An increase in dislocation density as well as increased diffusivity of Mn and Si significantly enhances the precipitation kinetics of the radiation-induced phases within this model.

1. Introduction

Austenitic stainless steels (ASSs) including 304, 316 and 347 grades are widely used for the core components of reactor pressure vessels in light water reactors (LWRs) due to their relatively high strength and good fracture toughness. These components experience significant neutron irradiation fluence during the service lifetime in LWRs, which leads to microstructural changes, phase instability and property degradation of the components [1,2]. In addition, compositional changes due to radiation-induced segregation (RIS) are usually observed in irradiated ASS components [3]. Radiation-induced defects diffuse to sinks such as grain boundaries during irradiation, and the excess defect fluxes to sinks causes non-equilibrium segregation of solute atoms due to an inverse Kirkendall effect and an interstitial association mechanism [4]. The RIS behavior of Cr and Ni in irradiated ASSs is well established, in which Cr depletes at grain boundaries while Ni is enriched [5,6]. The Cr and Ni segregation behavior is well explained by a modified inverse Kirkendall effect [7]. Si is also generally observed to enrich at grain boundaries in irradiated ASSs, which is usually explained by an interstitial association mechanism [8]. In addition to grain boundaries, RIS has been observed at voids and Frank loops in irradiated ASSs [9].

In LWR environments, the precipitation of second phases can take place under the combined effects of temperature, increased defect concentration and locally varying compositional domains due to RIS, and the second phase precipitate distributions clearly

* Corresponding author at: High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea. Tel.: +82 2 958 6760.
E-mail address: jhshim@kist.re.kr (J.-H. Shim).

http://dx.doi.org/10.1016/j.jnucmat.2015.04.013
0022-3115/

influence the hardening and embrittlement of the components [3]. Radiation-induced phases (RIPs) are precipitates that appear only under irradiation but not for corresponding thermal conditions [3]. γ′ and G phases are the typical RIPs observed in ASSs [10–20]. Of the various grades of ASSs, 316 may be the most susceptible to the formation of γ′ and G phases due to the higher Ni content. γ′ is an A_3B type intermetallic compound with an ordered fcc crystal structure ($L1_2$) and usually appears as Ni_3Si in irradiated ASSs. Radiation-induced γ′ has been observed to form near Frank loops in a temperature range between 300 and 500 °C in both 316 and Ti-stabilized 316 ASSs [17]. G phase is a complex silicide, $M_6Ni_{16}Si_7$ (M = Ti, Nb, Mn, Fe and/or Cr) with an fcc crystal structure (A1). Although G phase as a RIP was reported first in irradiated Ti- and Nb-stabilized 316 ASSs [12,17], further studies revealed that G phase is also observed, although at relatively low volume fractions, during irradiation in a 316 ASS [13,14,16,17]. Radiation-induced G phase has been observed to form near voids in a temperature range of 400–650 °C [17]. Further, a recent study indicates Ni and Si segregation to dislocation lines and loops in a proton irradiated 304 ASS, and that the dislocation can act as a RIP nucleation site [21].

In addition to experimental observations, there has been recent effort to simulate the precipitation kinetics in ASSs during aging by combining classical nucleation theory with growth equations from diffusion theory or the thermodynamic extremum principle [22–24]. These efforts were successful in providing a reasonably accurate prediction of the precipitation sequence, the precipitate phase fraction and precipitate size in ASSs, compared with experimental observations. However, no currently published study has predicted the precipitation kinetics of RIPs in ASSs.

The purpose of this study is to simulate the long-term evolution of precipitates in 316 and Ti-stabilized 316 ASSs considering the RIS effect using a numerical model based on classical nucleation theory and evolution equations derived from the thermodynamic extremum principle. Special attention is given to the precipitation kinetics of γ′ and G phases.

2. Computational details

The composition of a 316 ASS for the simulation was determined according to Refs. [13,16], and is shown in Table 1. A Ti-stabilized 316 ASS contains a small amount of Ti to prevent the formation of $M_{23}C_6$, which is responsible for sensitization. The composition of solute elements as a result of RIS at 5, 10 or 20 dpa was determined according to the measurements of grain boundary compositions in irradiated 316 ASSs in the literature [20,25–45]. The content of Cr, Ni and Si was taken from the average values of the data at various dose levels compiled in the literature [25–45]. It should be noted that the Si content measured by atom probe tomography (APT) [37–39,42,44] is usually larger than that measured by transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDS) [25,26,32]. This is presumably because APT provides a higher spatial resolution than TEM–EDS, which can detect more localized segregation of Si. The content of Mn, Mo and Ti was set constant irrespective of radiation dose using the results of Jiao and Was [20], Ohnuki et al. [25], Kenik et al. [27], Kato et al. [29], Kasahara et al. [32], Fukuya [42] and Hatakeyama et al. [44], as the dependence of the segregation behavior of Mn, Mo and Ti on dose has not been well established.

In addition to the calculation of the phase equilibria (e.g., equilibrium precipitation fractions) in type 316 ASSs, the simulation of the precipitate evolution in these steels has been performed with the thermo-kinetic software package MatCalc (version 5.61, release 0.006) developed by Kozeschnik et al. [46,47]. This model treats the kinetics of microstructural processes based on classical nucleation theory and evolution equations for the radius and composition of each precipitate derived from the thermodynamic extremum principle. The details of the basic principles composing MatCalc are given in Ref. [48]. We should mention that the thermodynamic calculation and the kinetic simulation are not spatially resolved, and thus are not performed for all regions in the steel. Instead, we have selected representative compositions that represent localized spatial regions, with different compositions than the bulk as a result of RIS. In such regions near strong defect sinks such as grain boundaries, dislocations or voids, RIS can provide a thermodynamic driving force for the formation of RIPs as locally stable phases. During the calculation and simulation, the thermodynamic and kinetic data for all phases, except for γ′ and G phases, were calculated from the MatCalc thermodynamic database 'mc_fe' (version 2.003) and the MatCalc mobility database 'mc_fe' (version 2.006), respectively [49]. The thermodynamic data for γ′ was taken from the thermodynamic assessment of the Ni–Si–Ti system by Tokunaga et al. [50]. G phase was modeled as $(Mn,Ti)_6Ni_{16}Si_7$ considering the solubility between Mn and Ti. The thermodynamic data for $Mn_6Ni_{16}Si_7$ and $Ti_6Ni_{16}Si_7$ were taken from the assessments of Hu et al. [51] and Tokunaga et al. [50], respectively. The thermodynamic parameters for γ′ and G phases used in the present work are listed in Table 2.

The matrix phase defined in the simulation is austenite. The partial transformation of the matrix into ferrite at low temperatures, which is known to be accelerated under irradiation conditions [17], was not considered in the model. Also, it is assumed that the composition is maintained uniform across the matrix and does not change with time. The grain size of austenite was assumed to be 50 μm, which is in the range obtained after conventional thermo-mechanical treatments of a 316 ASS [52]. The dislocation density of the austenite matrix is assumed to be 10^{13} m^{-2}, according to the measured data on solution annealed ASSs [53].

$M_{23}C_6$, M_6C, MX, Laves, χ, σ, γ′ and G phases were included in the simulation as possible precipitates. For the crystal structure and chemical composition of these precipitates, see the review by Sourmail [54]. The nucleation sites of the χ and σ phases were set to be grain boundaries, those of Laves phase and MX were set to dislocations and those of $M_{23}C_6$ and M_6C were set to both grain boundaries and dislocations, according to information in the literature [22,55]. The nucleation sites of γ′ and G phases were set to dislocations, as γ′ and G phases are known to nucleate mainly at Frank loops and voids, respectively, inside grains [17]. Although a recent study [20] reported that there is a tendency for the formation of Ni/Si-rich clusters before the formation of γ′ and G phases, this clustering tendency was not reflected in this simulation due to the limit of classical nucleation theory. The diffusivity ratio between precipitate and matrix, which influences the kinetics of

Table 1
Compositions of type 316 austenitic stainless steels (wt.%).

	Fe	Cr	Ni	Mo	Mn	Si	(Ti)	C	N
316	Bal.	17	13	2.2	1.8	0.6	(0.2)	0.05	0.03
Segregation at 5 dpa	Bal.	14 ± 2	18 ± 2	1	1	3 ± 2	(0.5)	0.05	0.03
Segregation at 10 dpa	Bal.	12 ± 1	21 ± 4	1	1	5 ± 1.5	(0.5)	0.05	0.03
Segregation at 20 dpa	Bal.	11 ± 2	24 ± 2	1	1	6	(0.5)	0.05	0.03